

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY  
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

30 SEP 2004

Applicant's or agent's file reference BP105724		FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/FI 2003/000251	International filing date (day/month/year) 01.04.2003	Priority date (day/month/year) 02.04.2002	
International Patent Classification (IPC) or national classification and IPC C01G 23/053, B01J 21/06			
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- This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.
- This report is also accompanied by ANNEXES, comprising:
  - ☒ (sent to the applicant and to the International Bureau) a total of 2 sheets, as follows:
    - ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
    - ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
  - ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) \_\_\_\_\_, containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

- |                                     |              |   |
|-------------------------------------|--------------|---|
| <input checked="" type="checkbox"/> | Box No. I    | Basis of the report   |
| <input type="checkbox"/>            | Box No. II   | Priority  |
| <input type="checkbox"/>            | Box No. III  | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability  |
| <input type="checkbox"/>            | Box No. IV   | Lack of unity of invention  |
| <input checked="" type="checkbox"/> | Box No. V    | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| <input type="checkbox"/>            | Box No. VI   | Certain documents cited   |
| <input type="checkbox"/>            | Box No. VII  | Certain defects in the international application  |
| <input type="checkbox"/>            | Box No. VIII | Certain observations on the international application   |

Date of submission of the demand 20.10.2003	Date of completion of this report 30.06.2004
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# INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI 2003/000251

## Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on a translation from the original language into the following language \_\_\_\_\_, which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3 and 23.1(b))  
☐ publication of the international application (under Rule 12.4)  
☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

☐ the international application as originally filed/furnished

☒ the description:

pages 1-11 as originally filed/furnished

pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_

pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_

☒ the claims:

pages \_\_\_\_\_ as originally filed/furnished

pages\* \_\_\_\_\_ as amended (together with any statement) under Article 19

pages\* 15-16 received by this Authority on 20.10.2003

pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_

☐ the drawings:

pages \_\_\_\_\_ as originally filed/furnished

pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_

pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_

☐ a sequence listing and/or any related table(s) – see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_

☐ the claims, Nos. \_\_\_\_\_

☐ the drawings, sheets/figs \_\_\_\_\_

☐ the sequence listing (*specify*): \_\_\_\_\_

☐ any table(s) related to the sequence listing (*specify*): \_\_\_\_\_

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

☐ the description, pages \_\_\_\_\_

☐ the claims, Nos. \_\_\_\_\_

☐ the drawings, sheets/figs \_\_\_\_\_

☐ the sequence listing (*specify*): \_\_\_\_\_

☐ any table(s) related to the sequence listing (*specify*): \_\_\_\_\_

\* If item 4 applies, some or all of those sheets may be marked "superseded."

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/FI 2003/000251

**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	<u>1-15</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-15</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-15</u>	YES
	Claims		NO

**2. Citations and explanations (Rule 70.7)**

Most relevant documents cited in the International Search Report:

D1: EP 0 675 086 A2

D2: Suzuko Yamazaki et al: "Effect of sulphate ions for sol-gel synthesis of titania photocatalyst", Applied Catalysis A: General, Vol 2, 2001, pp 97-102.

D3: WO 99/43616

D4: Database WPI, AN 1998-524530 & JP 10230169

D5: EP 0924 164 A2

**METHOD CLAIMS 1-9:**

D1 discloses a process for producing particles of titanium oxide for use as photocatalysts. According to example 3 in D1 (page 8-9), a solution of titanyl sulphate, i.e. titanium oxysulphate, was hydrolysed at 85 °C. The hydrolysis product was filtered and washed to obtain a wet cake, which was dried in order to obtain anatase-type titanium oxide fine particle powders. Thereafter, the particles were subjected to thermal and hydrothermal treatments. It is further mentioned in D1 that a seed may be present in the solution of titanyl sulphate (page 3, lines 55-57), and that the titanium oxide fine particles may be various titanium oxides, e.g. hydrous titanium oxide (page 3, lines 22-24).

Thus, the main difference between the process according to present claim 1 and the process according to D1 is that the product of the process according to claim 1 has a sulphur content of 1-5%. According to the description, the observed high catalytic activity of the product is related to the

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## Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: Box V

sulphur content. D1 does not recognise a relation between sulphur content and catalytic activity. The sulphur content is not even mentioned in D1. Further, the prior art found during the search reveals no  $\text{TiO}_2$  photocatalyst produced by a sulphate process with a sulphur content between 1-5%. The sulphur content of commercial titanium dioxide is 0.3-1.0 %, according to D3 (table 9).

Thus, there is no indications in the prior art, that would lead a skilled man towards the invention as defined in claim 1.

Accordingly, the invention according to claim 1 and dependent claims 2-9 is novel and considered to involve an inventive step.

PRODUCT CLAIMS 10-12:

D2 (refer to abstract, table 1 and fig.2) discloses a  $\text{TiO}_2$  photocatalyst with an S-content of 1.52 and 2.74 wt% and specific surface area of 138, 204 and 241  $\text{m}^2/\text{g}$ , which is prepared by peptization of titanium alkoxide in nitric acid, dialysis, concentration of the obtained sol to gel, drying and firing, i.e. a process different from the modified sulphate process disclosed in the present application.

Thus, the photocatalyst according to present claim 10 differs from those disclosed in D2 by the production method. The production method according to the present application can be expected to impart distinctive characteristics on the final product in relation to D2, in terms of photocatalytic activity.

Therefore, the subject matter of claim 10 and dependent claims 11-12 is considered novel and inventive over D2 (cf PCT Guidelines 5.26 - 5.27).

D3 (refer to page 3, lines 10-26 and tables 7 and 9) discloses  $\text{TiO}_2$  with a specific surface area of up to 240  $\text{m}^2/\text{g}$  and sulphur content of 0.04 - 0.24 wt% (or 0.12 - 0.72 calculated as  $\text{SO}_4^{2-}$ ), which is prepared by the sulphate process.

D4 discloses photocatalyst powder which contains fine titanium

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## Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: BOX V

dioxide particles with specific surface areas of 130-350 m<sup>2</sup>/g, prepared by the sulphate process. D4 is silent about the sulphur content, but it may be assumed that the sulphur content is about 0.3 - 1.0 wt%, since according to D3, the sulphur content of commercial TiO<sub>2</sub> is 0.3-1.0 wt%.

The photocatalyst according to present claim 10 differs from those disclosed in D3-D4 by the sulphur content, which, as mentioned above, is related to the observed high catalytic activity.

Therefore, the invention according to claims 10-12 is novel and considered inventive also over D3 and D4.

It may be noted that since claims 1 and 10 are considered inventive, D5, which relates to doping of titania catalysts with chromium or iron ions in order to obtain catalysts utilizable in visible light range (cf present claims 7-9 and 12), is no longer considered relevant.

USE CLAIMS 13-15:

The invention according to claims 13-15 is considered to fulfil the novelty and inventive step criteria, since the invention according to claims 1-12 do.

Finally, the claimed invention is considered to be industrially applicable.

## Claims

1. A method for preparing a photocatalyst containing titanium dioxide, **characterised** in that from an acid solution containing titanium oxysulphate at a temperature under the boiling point of the solution is precipitated by addition of chrystal nuclei a sulphurous titanium dioxide hydrate precipitate, said precipitate being separated and subsequently subjected to thermal treatment in order to obtain a crystalline product with a sulphur content of 1 to 5 %.
2. A method as defined in claim 1, **characterised** in that the precipitation is conducted without addition of base.
3. A method as defined in claim 1 or 2, **characterised** in that the precipitation is conducted in a temperature range from 70 to 100 °C.
4. A method as defined in claim 3, **characterised** in that the crystal nuclei are anatase.
5. A method as defined in any of the preceding claims, **characterised** in that the precipitate separated from the solution is calcinated in air in the temperature range from 100 to 500 °C, preferably 200 to 500 °C.
6. A method as defined in any of the preceding claims, **characterised** in that the solution containing titanium oxysulphate is obtained by reacting ilmenite and sulphuric acid, by dissolving the sulphate thus formed and by removing at least part of the iron from the solution by reduction into ferrous form and crystallisation.
7. A method as defined in claim 6, **characterised** in that ferric iron is left in the solution, so that the titanium dioxide hydrate precipitate obtained contains iron.
8. A method as defined in any of the preceding claims, **characterised** in that a chromium(III)compound is added to the precipitate before the thermal treatment.
9. A method as defined in any of the preceding claims, **characterised** in that an iron compound is added to the precipitate before the thermal treatment.

10. A photocatalyst obtained by a method according to any of the preceding claims, the photocatalyst containing titanium dioxide, **characterised** in that the crystalline particulate product has a specific surface area in the range from 100 to 250 m<sup>2</sup>/g and that the product contains 1 to 5%, preferably 1 to 4% of sulphur.

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11. A photocatalyst as defined in claim 10, **characterised** in that the major portion of titanium dioxide is in anatase form.

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12. A photocatalyst as defined in claim 10 or 11, **characterised** in that the product contains 0.05 to 2% of chromium, preferably 0.1 to 1%, and 0.05 to 0.3% of iron, preferably 0.1 to 1.5%.

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13. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst operating at visible light wavelengths.

14. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst in the decomposition of organic compounds or microorganisms.

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15. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst in a coating composition.